

Irreversible Circulation of Fluctuation and Entropy Production

Hiroyuki TOMITA¹ and Mitsusada M. SANO²

¹*Interdisciplinary Graduate School of Science and Engineering,
Kinki University,
Higashi-Osaka 577-8502, Japan*

²*Graduate School of Human and Environmental Studies,
Kyoto University,
Kyoto 606-8501, Japan*

Physical and chemical stochastic processes described by the master equation are investigated. The system-size expansion, called the Ω -expansion, transforms the master equation to the corresponding Fokker-Planck equation. In this paper, we examine the entropy production for both the master equation and the corresponding Fokker-Planck equation. For the master equation, the exact expression of the entropy production was recently derived by Gaspard using Kolmogorov-Sinai entropy (J.Stat.Phys. **117** (2004), 599 [Errata; **126** (2006), 1109]). Although Gaspard's expression is derived from a stochastic consideration, it should be noted that it coincides with the thermodynamical expression. For the corresponding Fokker-Planck equation, by using the detailed imbalance relation, which appears in the process of deriving the fluctuation theorem through the Onsager-Machlup theory, the entropy production is expressed in terms of the *irreversible circulation of fluctuation*, which was proposed by Tomita and Tomita (Prog.Theor.Phys. **51** (1974), 1731 [Errata; **53** (1975), 1546b]). However, this expression for the corresponding Fokker-Planck equation differs from that of the entropy production for the master equation. This discrepancy is due to the difference between the master equation and the corresponding Fokker-Planck equation, namely the former treats discrete events, but the latter equation is an approximation of the former one. In fact, in the latter equation, the original discrete events are smoothed out. To overcome this difficulty, we propose a hypothetical *path weight principle*. By using this principle, the modified expression of the entropy production for the corresponding Fokker-Planck equation coincides with that of the master equation (i.e., the thermodynamical expression) for a simple chemical reaction system and a diffusion system.

§1. Introduction

Theories on nonequilibrium systems near equilibrium have been successful. In fact, a number of landmarks have been achieved in nonequilibrium statistical physics, such as Onsager's reciprocal relation^{1),2)} and the Kubo formula.³⁾ However, there has been no satisfactory theory on nonequilibrium steady states (NESS) until the recent discovery of the fluctuation theorem focused on the NESS.⁴⁾⁻⁹⁾ With such developments, the study of the NESS (i.e., the characterization of the NESS) is a little revival. The fluctuation theorem gives us some indications of how to investigate the NESS. However, theorists consider individual problems from their perspective. A unified viewpoint is lacking in the present study of the NESS.

In this paper, as an attempt to improve the present situation, we construct a theory of the NESS for certain stochastic processes, i.e., the master equation and the Fokker-Planck equation. The entropy production for these equations is

examined. For the master equation, in a pioneering work by Schnakenberg,¹⁰⁾ an exact expression of the entropy production for the master equation was derived. Recently Gaspard also derived this equation starting from Kolmogorov-Sinai (KS) entropy.¹¹⁾ His formula is

$$\langle \sigma_e \rangle = \frac{1}{\tau} \Delta S_i = h^R - h, \quad (1.1)$$

where h is the KS entropy and h^R is the time-reversed KS entropy. Throughout this paper, we set the Boltzmann constant $k_B = 1$ and we use the following notation for the entropy production, namely, the thermodynamical entropy production $\sigma_{e,\text{th}}$ and the stochastic averaged entropy production $\langle \sigma_e \rangle$. Equation (1.1) coincides with Schnakenberg's result. It should be noted that it also agrees with the thermodynamical result. Thus, the entropy production defined by the stochastic process coincides with the corresponding thermodynamical entropy production.

In the 1970s, systematic studies were carried out on the master equation.^{12),13)} Kubo et al.¹²⁾ applied the system-size expansion, called the Ω -expansion, which was developed by van Kampen,¹⁴⁾ to the master equation. They derived the corresponding Fokker-Planck equation and analyzed the behavior of the fluctuation. Later Tomita and Tomita developed Kubo et al.'s work and emphasized the importance of the circulation of fluctuation in nonequilibrium states.¹³⁾ In particular, in the NESS, they showed that the probability flow circulates. Successively, Tomita et al. applied the Onsager-Machlup theory^{15),16)} to the result of Ref. 13).¹⁷⁾ Unfortunately, in Refs. 13) and 17), the entropy production was not investigated.

Recently, Taniguchi and Cohen extended the Onsager-Machlup theory to several Langevin systems^{19)–21)} and derived a fluctuation theorem for them. A key relation in the fluctuation theorem is the *detailed imbalance relation* (they called it the nonequilibrium detailed balance relation), i.e., the violation of the detailed balance relation. In this paper, on the basis of this key relation, we shall evaluate the entropy production of the Fokker-Planck equation derived from the master equation. However, this entropy production does not coincide with the entropy production for the original master equation. The reason for this will be examined in detail. The difference between them is due to the fact that our master equation treats discrete events, but the Fokker-Planck equation is an approximation of it. In the Fokker-Planck equation, the original discrete events are smoothed out. To overcome this difficulty, we propose a *path weight principle*. Using this path weight principle, the modified entropy production for the corresponding Fokker-Planck equation coincides with that of the original master equation, which is simply the thermodynamical result.

The organization of this paper is as follows. In § 2, the master equation is introduced and the expression for its entropy production is given. After that, the master equation is transformed to the corresponding Fokker-Planck equation by the Ω -expansion. In § 3, the Onsager-Machlup theory is applied to the corresponding Fokker-Planck equation. By calculating the path probability, the detailed imbalance relation is derived. The entropy production term is also determined. In § 4, two example cases are considered. One is a chemical reaction network. The other is a

one-dimensional diffusion system. For both cases, the entropy production disagrees with the thermodynamical result. In § 5, to improve the result of the previous section, the *path weight principle* is proposed and applied to the two examples. As a result, the modified entropy production based on the path weight principle coincides with the thermodynamical result. In § 6, we summarize the results.

§2. Master equation, Ω -expansion, and Fokker-Planck equation

In this section, we review Gaspard's result¹¹⁾ and the results of the 1970s.^{12)–14), 17)}

Our starting point is the master equation. The master equation describes physical and chemical processes, such as diffusion systems and chemical reaction networks. In § 4, we give two such examples. The master equation is given by

$$\frac{\partial}{\partial t}P(\mathbf{X};t) = - \sum_{\mathbf{X}'} W(\mathbf{X} \rightarrow \mathbf{X}')P(\mathbf{X};t) + \sum_{\mathbf{X}'} W(\mathbf{X}' \rightarrow \mathbf{X})P(\mathbf{X}';t), \quad (2.1)$$

where $\mathbf{X} = (X_1, X_2, \dots, X_N)^t$ is the variable of the state. $P(\mathbf{X};t)$ is the probability distribution that the system is in state \mathbf{X} at time t . $W(\mathbf{X} \rightarrow \mathbf{X}')$ is the transition probability rate, i.e., the probability that the system performs a transition from state \mathbf{X} to state \mathbf{X}' in a unit time. The entropy production for this master equation was recently calculated by Gaspard using KS entropy.¹¹⁾ Its expression is given by

$$\langle \sigma_e \rangle = \frac{1}{2} \sum_{\mathbf{X}, \mathbf{X}'} \{ P^{\text{st}}(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}') - P^{\text{st}}(\mathbf{X}')W(\mathbf{X}' \rightarrow \mathbf{X}) \} \ln \frac{P^{\text{st}}(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}')}{P^{\text{st}}(\mathbf{X}')W(\mathbf{X}' \rightarrow \mathbf{X})}, \quad (2.2)$$

where $P^{\text{st}}(\mathbf{X})$ is the probability distribution for the NESS. This expression is obtained by rewriting Eq. (1.1) and is equivalent to the expression originally obtained by Schnakenberg.¹⁰⁾ Thus, in this paper, we call Eq. (2.2) the Schnakenberg-Gaspard expression. In addition, it should be noted that this expression is simply the thermodynamical expression. For chemical reaction systems, Eq. (2.2) is rewritten in the form of the sum of the products of the reaction rate and the affinity. Thus, the stochastic consideration gives the thermodynamical result for this problem.

Here the connection between the Schnakenberg-Gaspard expression, i.e., Eq. (2.2), and the fluctuation theorem (i.e., the path probability ratio) is shown. The path probability ratio between the forward path and the reverse path is given by

$$\frac{P^{\text{st}}(\mathbf{A})W_{\text{path}}(\mathbf{A} \rightarrow \mathbf{B})}{P^{\text{st}}(\mathbf{B})W_{\text{path}}(\mathbf{B} \rightarrow \mathbf{A})} = \exp[\Sigma(\mathbf{A} \rightarrow \mathbf{B})], \quad (2.3)$$

where $\Sigma(\mathbf{A} \rightarrow \mathbf{B})$ is the entropy production for the path $\mathbf{A} \rightarrow \mathbf{B}$. This relation is a key relation in the derivation of the fluctuation theorem. If the time-reversal symmetry is satisfied, then the right-hand side of Eq. (2.3) is 1. Now we assume that the forward path is given by

$$\mathbf{A} \rightarrow \mathbf{X}^{(1)} \rightarrow \mathbf{X}^{(2)} \rightarrow \dots \rightarrow \mathbf{X}^{(T-1)} \rightarrow \mathbf{B}. \quad (2.4)$$

The path probability is given by the step-by-step transition probabilities as

$$W_{\text{path}}(\mathbf{A} \rightarrow \mathbf{B}) = W(\mathbf{A} \rightarrow \mathbf{X}^{(1)})W(\mathbf{X}^{(1)} \rightarrow \mathbf{X}^{(2)}) \dots W(\mathbf{X}^{(T-1)} \rightarrow \mathbf{B}), \quad (2.5)$$

namely in a Markov chain. Let the transition probability be

$$W^{(t)}(\mathbf{A} \rightarrow \mathbf{X}') = \sum_{\mathbf{X}^{(1)}} \sum_{\mathbf{X}^{(2)}} \cdots \sum_{\mathbf{X}^{(t-1)}} W_{\text{path}}(\mathbf{A} \rightarrow \mathbf{X}'). \quad (2.6)$$

The path probability ratio between the forward and reverse paths is given by

$$\begin{aligned} & \log \frac{P^{\text{st}}(\mathbf{A})W_{\text{path}}(\mathbf{A} \rightarrow \mathbf{B})}{P^{\text{st}}(\mathbf{B})W_{\text{path}}(\mathbf{B} \rightarrow \mathbf{A})} \\ &= \sum_{t=0}^{T-1} \log \frac{P^{\text{st}}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)} \rightarrow \mathbf{X}^{(t+1)})}{P^{\text{st}}(\mathbf{X}^{(T-t)})W(\mathbf{X}^{(T-t)} \rightarrow \mathbf{X}^{(T-t-1)})} \\ &= \log \frac{P^{\text{st}}(\mathbf{A})W(\mathbf{A} \rightarrow \mathbf{X}^{(1)})}{P^{\text{st}}(\mathbf{X}^{(1)})W(\mathbf{X}^{(1)} \rightarrow \mathbf{A})} + \log \frac{P^{\text{st}}(\mathbf{X}^{(T-1)})W(\mathbf{X}^{(T-1)} \rightarrow \mathbf{B})}{P^{\text{st}}(\mathbf{B})W(\mathbf{B} \rightarrow \mathbf{X}^{(T-1)})} \\ & \quad + \sum_{t=1}^{T-2} \log \frac{P^{\text{st}}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)} \rightarrow \mathbf{X}^{(t+1)})}{P^{\text{st}}(\mathbf{X}^{(t+1)})W(\mathbf{X}^{(t+1)} \rightarrow \mathbf{X}^{(t)})}. \end{aligned} \quad (2.7)$$

Before taking the limit $T \rightarrow \infty$, the path average is obtained. Then we have

$$\begin{aligned} \langle \Sigma(\mathbf{A} \rightarrow \mathbf{B}) \rangle &= (\text{both end terms}) \\ & \quad + \sum_{t=1}^{T-2} \sum_{\text{all paths}} P^{\text{st}}(\mathbf{A})W^{(t)}(\mathbf{A} \rightarrow \mathbf{X}^{(t)})W(\mathbf{X}^{(t)} \rightarrow \mathbf{X}^{(t+1)}) \\ & \quad \times W(\mathbf{X}^{(t+1)} \rightarrow \mathbf{B}) \log \frac{P^{\text{st}}(\mathbf{X}^{(t)})W(\mathbf{X}^{(t)} \rightarrow \mathbf{X}^{(t+1)})}{P^{\text{st}}(\mathbf{X}^{(t+1)})W(\mathbf{X}^{(t+1)} \rightarrow \mathbf{X}^{(t)})}. \end{aligned} \quad (2.8)$$

For the NESS, we assume that

$$\sum_{\mathbf{A}} P^{\text{st}}(\mathbf{A})W^{(t)}(\mathbf{A} \rightarrow \mathbf{X}) = P^{\text{st}}(\mathbf{X}). \quad (2.9)$$

We use the Bayes relation

$$W(\mathbf{X}^{(t+1)} \rightarrow \mathbf{B}) = P^{\text{st}}(\mathbf{X}^{(t+1)})^{-1} \overline{W}(\mathbf{X}^{(t+1)} \rightarrow \mathbf{B}) P^{\text{st}}(\mathbf{B}), \quad (2.10)$$

and

$$\sum_{\mathbf{B}} \overline{W}(\mathbf{X}^{(t+1)} \rightarrow \mathbf{B}) P^{\text{st}}(\mathbf{B}) = P^{\text{st}}(\mathbf{X}^{(t+1)}), \quad (2.11)$$

where the bar denotes the destined conditional probability. Thus, the average entropy production is given by

$$\begin{aligned} \langle \sigma_e \rangle &= \lim_{T \rightarrow \infty} \frac{1}{T} \langle \Sigma(\mathbf{A} \rightarrow \mathbf{B}) \rangle \\ &= \sum_{\mathbf{X}, \mathbf{X}'} P^{\text{st}}(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}') \log \frac{P^{\text{st}}(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}')}{P^{\text{st}}(\mathbf{X}')W(\mathbf{X}' \rightarrow \mathbf{X})}. \end{aligned} \quad (2.12)$$

Equation (2.12) is simply the Schnakenberg-Gaspard expression, i.e., Eq. (2.2). Throughout this paper, we call this relation the detailed imbalance expression of entropy production. The fluctuation theorem involves the asymptotic behavior of long-time fluctuation. However, note that the entropy production in the NESS is determined by the detailed imbalance of short-time fluctuation in this formula.

As in Refs. 12) and 14), the Ω -expansion is used for Eq. (2.1). Here Ω is a variable that is related to the system size. For chemical reaction systems, Ω should be on the order of the Avogadro number or the volume of the system. We set

$$W(\mathbf{X} \rightarrow \mathbf{X} + \mathbf{r}) = \Omega w\left(\frac{\mathbf{X}}{\Omega}; \mathbf{r}\right) \quad (2.13)$$

and scale the variable \mathbf{X} ,

$$\mathbf{x} = \frac{\mathbf{X}}{\Omega}. \quad (2.14)$$

The master equation is rewritten as

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\Omega \sum_{\mathbf{r}} (1 - e^{-\epsilon \mathbf{r} \cdot \frac{\partial}{\partial \mathbf{x}}}) w(\mathbf{x}; \mathbf{r}) p(\mathbf{x}; t), \quad (2.15)$$

where $\epsilon = 1/\Omega$ is used. The probability distribution is now scaled as

$$\Omega^N P(\mathbf{X}; t) = p(\mathbf{x}; t). \quad (2.16)$$

Expanding the right-hand side of Eq. (2.15) in terms of ϵ , we obtain the following equation:

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = \sum_{n=1}^{\infty} \frac{\epsilon^{n-1}}{n!} \left(-\frac{\partial}{\partial \mathbf{x}} \right)^n \cdot \mathbf{c}_n(\mathbf{x}) p(\mathbf{x}; t), \quad (2.17)$$

where

$$\mathbf{c}_n(\mathbf{x}) = \sum_{\mathbf{r}} (\mathbf{r})^n w(\mathbf{x}; \mathbf{r}) \quad (2.18)$$

is the n th moment of the transition probability rate. In particular, $\mathbf{c}_1(\mathbf{x})$ and $\mathbf{c}_2(\mathbf{x})$ are given by

$$\mathbf{c}_{1,k}(\mathbf{x}) = \sum_{\mathbf{r}} r_k w(\mathbf{x}; \mathbf{r}), \quad \mathbf{c}_{2,kl}(\mathbf{x}) = \sum_{\mathbf{r}} r_k r_l w(\mathbf{x}; \mathbf{r}). \quad (2.19)$$

By considering the lowest order of ϵ , we obtain the following equation:

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{c}_1(\mathbf{x}) p(\mathbf{x}; t) + \frac{\epsilon}{2} \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{c}_2(\mathbf{x}) p(\mathbf{x}; t). \quad (2.20)$$

Here the \mathbf{x} -dependence of $\mathbf{c}_2(\mathbf{x})$ is explicitly considered. Then we obtain

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbf{c}_1(\mathbf{x}) - \frac{\epsilon}{2} \mathbf{h}(\mathbf{x}) - \frac{\epsilon}{2} \mathbf{c}_2(\mathbf{x}) \cdot \frac{\partial}{\partial \mathbf{x}} \right] p(\mathbf{x}; t), \quad (2.21)$$

where

$$\mathbf{h}(\mathbf{x}) = \mathbf{c}_2(\mathbf{x}) \cdot \frac{\overleftarrow{\partial}}{\partial \mathbf{x}}. \quad (2.22)$$

Here the term $\epsilon \mathbf{h}(\mathbf{x})/2$ can be neglected, because compared with \mathbf{c}_1 , it is on the order of ϵ . For later use,^{*)} we set

$$\mathbf{D}(\mathbf{x}) = \frac{1}{2} \mathbf{c}_2(\mathbf{x}), \quad (2.23)$$

which is the diffusion-constant matrix in the probability space. If the fluctuation is assumed to be normal,¹²⁾ i.e.,

$$p(\mathbf{x}; t) = A(\mathbf{x}; t) e^{-\Omega \phi(\mathbf{x}; t)}, \quad (2.24)$$

the probability distribution is well approximated as a Gaussian distribution on the order of ϵ ,

$$\phi(\mathbf{x}; t) = \frac{1}{2} (\mathbf{x} - \mathbf{y}(t))^t \cdot \boldsymbol{\sigma}^{-1} \cdot (\mathbf{x} - \mathbf{y}(t)). \quad (2.25)$$

Then we obtain the time evolution of $\mathbf{y}(t)$ and $\boldsymbol{\sigma}(t)$ as follows:

$$\frac{d\mathbf{y}}{dt} = \mathbf{c}_1(\mathbf{y}), \quad (2.26)$$

$$\frac{d\boldsymbol{\sigma}}{dt} = \mathbf{K} \cdot \boldsymbol{\sigma} + \boldsymbol{\sigma} \cdot \widetilde{\mathbf{K}} + \mathbf{c}_2(\mathbf{y}), \quad (2.27)$$

where

$$K_{kl}(\mathbf{y}) = \frac{\partial c_{1,k}(\mathbf{y})}{\partial y_l}. \quad (2.28)$$

The matrix elements of $\boldsymbol{\sigma}$ are given by

$$\sigma_{ij} = \int d\boldsymbol{\xi} \xi_i \xi_j \tilde{p}(\boldsymbol{\xi}; t), \quad (2.29)$$

where

$$\mathbf{x} = \mathbf{y}(t) + \epsilon^{1/2} \boldsymbol{\xi} \quad (2.30)$$

and $\tilde{p}(\boldsymbol{\xi}; t)$ is the probability distribution for $\boldsymbol{\xi}$. Thus, $\boldsymbol{\sigma}$ and \mathbf{g} correspond to the definitions in Ref. 13). Solving Eq. (2.26) and inserting its solution into $\mathbf{D}(\mathbf{x})$, we obtain $\mathbf{y}(t)$ and $\mathbf{D}(t)$. Therefore, as a result, we obtain the Fokker-Planck equation:

$$\frac{\partial}{\partial t} p(\mathbf{x}; t) = -\frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbf{c}_1(\mathbf{x}) - \epsilon \mathbf{D}(t) \cdot \frac{\partial}{\partial \mathbf{x}} \right] p(\mathbf{x}; t). \quad (2.31)$$

Hereafter we investigate this Fokker-Planck equation in detail.

From Eq. (2.31), several interesting properties for the NESS have been discovered.¹³⁾ The probability distribution for the NESS is given by

$$p^{\text{st}}(\mathbf{x}) = \frac{1}{\sqrt{(2\pi\epsilon)^N \det(\boldsymbol{\sigma}^{\text{st}})}} \exp[-\Omega \phi(\mathbf{x})], \quad (2.32)$$

where

$$\phi(\mathbf{x}) = \frac{1}{2} (\mathbf{x} - \langle \mathbf{x} \rangle)^t \cdot \mathbf{g}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \quad (2.33)$$

^{*)} Here we used the standard definition of \mathbf{D} , which is different from that in Ref. 13) by a factor of 1/2.

and

$$\mathbf{g}^{\text{st}} = (\boldsymbol{\sigma}^{\text{st}})^{-1}. \quad (2.34)$$

$\boldsymbol{\sigma}^{\text{st}}$ is the variance matrix of the probability distribution of the NESS. In this case, the phenomenological equation is given by

$$\begin{aligned} \mathbf{X} &= -\frac{\partial \phi}{\partial \mathbf{x}} \\ &= -\mathbf{g}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle). \end{aligned} \quad (2.35)$$

If $\mathbf{c}_1(\mathbf{x})$ is given as

$$\mathbf{c}_1(\mathbf{x}) = \mathbf{K}^{\text{st}} \cdot \mathbf{x} + \mathbf{c}, \quad (2.36)$$

(two examples in § 4 are discussed for this case), we have

$$\begin{aligned} \dot{\mathbf{x}} &= \mathbf{K}^{\text{st}} \cdot \mathbf{x} + \mathbf{c} \\ &= \mathbf{K}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \\ &= -\mathbf{L} \cdot \mathbf{X}. \end{aligned} \quad (2.37)$$

Here we have used the fact that $\dot{\mathbf{x}} = 0 \Rightarrow \langle \mathbf{x} \rangle = -(\mathbf{K}^{\text{st}})^{-1} \cdot \mathbf{c}$, where \mathbf{L} is the Onsager coefficient. Also we have the following relations,¹³⁾

$$\mathbf{L} = -\mathbf{K}^{\text{st}}(\mathbf{g}^{\text{st}})^{-1} = \mathbf{D}^{\text{st}} + \boldsymbol{\alpha}, \quad (2.38)$$

$$\begin{aligned} \boldsymbol{\alpha} &= -\mathbf{K}^{\text{st}} \boldsymbol{\sigma}^{\text{st}} - \mathbf{D}^{\text{st}} \\ &= \frac{1}{2}(\boldsymbol{\sigma}^{\text{st}} \widetilde{\mathbf{K}}^{\text{st}} - \mathbf{K}^{\text{st}} \boldsymbol{\sigma}^{\text{st}}). \end{aligned} \quad (2.39)$$

The matrix $\boldsymbol{\alpha}$ vanishes for the case that the detailed balance is satisfied, i.e., in equilibrium. However, for the NESS, $\boldsymbol{\alpha}$ is non zero in general. In addition, $\boldsymbol{\alpha}$ is an antisymmetric matrix. As shown in Ref. 13), $\boldsymbol{\alpha}$ is a measure of the circulation of fluctuation. Therefore, $\boldsymbol{\alpha}$ is called the *irreversible circulation of fluctuation*.

Now we set

$$\mathbf{v}(\mathbf{x}) = \dot{\mathbf{y}}(\mathbf{x}) + \mathbf{D}^{\text{st}} \cdot \nabla \phi(\mathbf{x}). \quad (2.40)$$

We call the vector \mathbf{v} the *irreversible circulation velocity*. If $\dot{\mathbf{y}}(\mathbf{x}) = \mathbf{K}^{\text{st}} \cdot \mathbf{x} + \mathbf{c}$, the irreversible circulation velocity can be rewritten as

$$\begin{aligned} \mathbf{v}(\mathbf{x}) &= \mathbf{K}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) + \mathbf{D}^{\text{st}} \cdot \nabla \phi(\mathbf{x}) \\ &= (\mathbf{K}^{\text{st}} + \mathbf{D}^{\text{st}} \mathbf{g}^{\text{st}}) \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \\ &= -\boldsymbol{\alpha} \cdot \nabla \phi(\mathbf{x}) \\ &= \boldsymbol{\alpha} \cdot \mathbf{X}(\mathbf{x}). \end{aligned} \quad (2.41)$$

Therefore, we have

$$\mathbf{v}(\mathbf{x}) = \mathbf{j}(\mathbf{x})/P^{\text{st}}(\mathbf{x}). \quad (2.42)$$

Here $\mathbf{j}(\mathbf{x})$ is the current of the probability. This relation was also obtained in Ref. 22).

In addition, the irreversible circulation $\boldsymbol{\alpha}$ is related to the breaking of the fluctuation-dissipation theorem. If the fluctuation-dissipation theorem is satisfied, i.e., $\boldsymbol{\alpha} = 0$, then

$$-\mathbf{K}^{\text{st}} \boldsymbol{\sigma}^{\text{st}} = \mathbf{D}^{\text{st}}. \quad (2.43)$$

The breaking of the fluctuation-dissipation theorem has recently been recognized for the corresponding Langevin system.¹⁸⁾

§3. Path probability and detailed imbalance relation

Following Tomita et al.,¹⁷⁾ we apply the Onsager-Machlup theory^{15),16)} to the Fokker-Planck equation, Eq. (2·31). The time evolution of the probability distribution can be written in terms of the transition probability.

$$p(\mathbf{x}; t) = \int d\mathbf{x}' F \left(\begin{array}{c} \mathbf{x} \\ t \end{array} \middle| \begin{array}{c} \mathbf{x}' \\ t_0 \end{array} \right) p(\mathbf{x}'; t_0). \quad (3·1)$$

$F(\dots)$ is the transition probability. For a short-time propagation, the transition probability is evaluated as

$$\begin{aligned} & F \left(\begin{array}{c} \mathbf{x} + \Delta\mathbf{x} \\ t + \Delta t \end{array} \middle| \begin{array}{c} \mathbf{x} \\ t \end{array} \right) \\ &= \frac{1}{\sqrt{(2\pi)^N \det(\mathbf{D}(t)) (\epsilon \Delta t)^N}} \\ & \times \exp \left[-\frac{\Delta t \Omega}{4} \left(\frac{\Delta\mathbf{x}}{\Delta t} - \dot{\mathbf{y}}(\mathbf{x}) \right)^t \cdot \mathbf{R} \cdot \left(\frac{\Delta\mathbf{x}}{\Delta t} - \dot{\mathbf{y}}(\mathbf{x}) \right) \right] + \mathcal{O}((\Delta t)^2), \end{aligned} \quad (3·2)$$

where $\mathbf{R} = \mathbf{D}^{-1}$. From Eq. (3·2), the Lagrangian for the path integral (i.e., the Onsager-Machlup function) is given by

$$\mathcal{L}(\dot{\mathbf{x}}, \mathbf{x}) = -\frac{\Omega}{4} (\dot{\mathbf{x}} - \dot{\mathbf{y}}(\mathbf{x}))^t \cdot \mathbf{R} \cdot (\dot{\mathbf{x}} - \dot{\mathbf{y}}(\mathbf{x})). \quad (3·3)$$

The path probability is given by

$$W_{\text{path}}(\{\mathbf{x}\}; A \rightarrow B) = \exp \left[\int_{t_0}^t ds \mathcal{L}(\dot{\mathbf{x}}^*(s), \mathbf{x}^*(s)) \right], \quad (3·4)$$

where $\mathbf{x}^*(s)$ is to be taken along a given path $A \rightarrow B$. We set $A = \mathbf{x}(t_0)$ and $B = \mathbf{x}(t)$. To calculate the path probability ratio, we evaluate the difference between the Lagrangians.

$$\mathcal{L}(\dot{\mathbf{x}}, \mathbf{x}) - \mathcal{L}(-\dot{\mathbf{x}}, \mathbf{x}) = \Omega \dot{\mathbf{x}} \cdot \mathbf{R} \cdot \dot{\mathbf{y}}(\mathbf{x}). \quad (3·5)$$

Here we assume that the probability distribution in the NESS is given by

$$p^{\text{st}}(\mathbf{x}) \propto \exp[-\Omega \phi(\mathbf{x})]. \quad (3·6)$$

Thus, we have

$$\mathcal{L}(\dot{\mathbf{x}}, \mathbf{x}) - \mathcal{L}(-\dot{\mathbf{x}}, \mathbf{x}) = -\Omega \dot{\phi}(\mathbf{x}) + \Omega \dot{\mathbf{x}} \cdot \mathbf{R}^{\text{st}} \cdot [\dot{\mathbf{y}}(\mathbf{x}) + \mathbf{D}^{\text{st}} \cdot \nabla \phi(\mathbf{x})], \quad (3·7)$$

in which we have used the relation $\dot{\phi}(\mathbf{x}) = \nabla \phi \cdot \dot{\mathbf{x}}$. Then for the NESS, we obtain

$$\frac{P^{\text{st}}(A) W_{\text{path}}(\{\mathbf{x}\}; A \rightarrow B)}{P^{\text{st}}(B) W_{\text{path}}(\{\mathbf{x}\}; B \rightarrow A)} = \exp \left[\Omega \int_A^B dt \dot{\mathbf{x}}^t \cdot \mathbf{R}^{\text{st}} \cdot \mathbf{v} \right]. \quad (3·8)$$

Similar relations were also obtained for Langevin systems by Taniguchi and Cohen,^{19)–21)*)} Seifert,²²⁾ and Chernyak et al.²³⁾ If the detailed balance relation is satisfied, the right hand side of eq. (3·8) is equal to 1, i.e., it is in equilibrium and the entropy production is zero, because $\alpha = 0$. It is known that compared with the Onsager-Machlup theory, the argument of the exponential function is related to the entropy production. Therefore, the argument of the exponential function on the right-hand side is the entropy production rate for the path $A \rightarrow B$. Thus, we finally obtain a stochastic form of the entropy production rate,

$$\sigma_e(\dot{\mathbf{x}}, \mathbf{x}) = \Omega \dot{\mathbf{x}}^t \cdot \mathbf{R}^{\text{st}} \cdot \mathbf{v}(\mathbf{x}). \quad (3.9)$$

Next, consider the average value of the entropy production term. As in the Onsager-Machlup theory, the most probable paths are categorized into two types, i.e., the forward evolution and the reverse evolution. For the forward evolution, the most probable path is given by

$$\dot{\mathbf{x}} = \mathbf{K}^{\text{st}} \cdot \mathbf{x} + \mathbf{c} = \mathbf{K}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle). \quad (3.10)$$

Inserting Eq. (3·10) into Eq. (3·9) gives

$$\sigma_e(\mathbf{x}) = \Omega \{ \mathbf{K}^{\text{st}} \cdot (\mathbf{x} - \langle \mathbf{x} \rangle) \}^t \cdot \mathbf{R}^{\text{st}} \alpha \cdot \mathbf{X}(\mathbf{x}). \quad (3.11)$$

Taking an average over the NESS, we obtain

$$\begin{aligned} \langle \sigma_e \rangle &= \int d\mathbf{x} P^{\text{st}}(\mathbf{x}) \sigma_e(\mathbf{x}) \\ &= -\text{Tr}(\alpha \mathbf{R}^{\text{st}} \alpha \mathbf{g}^{\text{st}}). \end{aligned} \quad (3.12)$$

This is the central result of this section, i.e., another form of the detailed imbalance expression. Note that the entropy production is expressed in terms of the irreversible circulation α . If in equilibrium, i.e., the detailed balance is satisfied, α is zero. Then, the entropy production vanishes. This is consistent with the physical requirement. It is important that the entropy production is expressed as a quadratic form of α .

§4. Examples

In this section, we check whether or not the derived expression of the entropy production coincides with the thermodynamical expression. Two examples are considered. One is a chemical reaction network. The other is a one-dimensional diffusion system.

4.1. Chemical reaction network

Let us consider the following simple case:



*) They called this relation the nonequilibrium detailed balance relation.

Here all rate constants are equal to κ . To maintain the steady state, the concentrations of the chemical species A and B are kept constant by reservoirs. This chemical reaction system is linear. Using Eqs. (2.28) and (2.36), the matrix \mathbf{K}^{st} and the vector \mathbf{c} are given by

$$\mathbf{K}^{\text{st}} = \kappa \begin{pmatrix} -2 & 1 \\ 1 & -2 \end{pmatrix}, \quad \mathbf{c} = \kappa \begin{pmatrix} \langle a \rangle \\ \langle b \rangle \end{pmatrix}, \quad (4.2)$$

where $\langle a \rangle = \langle A \rangle / \Omega$ and $\langle b \rangle = \langle B \rangle / \Omega$. Using Eq. (2.23) for \mathbf{D}^{st} , Eq. (2.28) for \mathbf{K}^{st} , and making the right-hand side of Eq. (2.27) equal to zero, we obtain the matrix $\boldsymbol{\sigma}^{\text{st}}$.

$$\boldsymbol{\sigma}^{\text{st}} = \frac{1}{3} \begin{pmatrix} 2\langle a \rangle + \langle b \rangle & 0 \\ 0 & \langle a \rangle + 2\langle b \rangle \end{pmatrix}. \quad (4.3)$$

Using Eq. (2.39), the matrix $\boldsymbol{\alpha}$ is given by

$$\boldsymbol{\alpha} = \frac{\kappa(\langle a \rangle - \langle b \rangle)}{6} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \quad (4.4)$$

The entropy production derived from the Fokker-Planck equation becomes

$$\begin{aligned} \langle \sigma_e \rangle &= -\text{Tr}(\boldsymbol{\alpha} \mathbf{R}^{\text{st}} \boldsymbol{\alpha} \mathbf{g}^{\text{st}}) \\ &= \kappa \frac{4(\langle a \rangle - \langle b \rangle)^2}{23\langle a \rangle^2 + 62\langle a \rangle \langle b \rangle + 23\langle b \rangle^2} \\ &\approx \frac{4\kappa(\langle a \rangle - \langle b \rangle)^2}{27(\langle a \rangle + \langle b \rangle)^2}. \end{aligned} \quad (4.5)$$

The last line is the approximation near equilibrium, i.e., $\langle a \rangle \sim \langle b \rangle$. We have employed an expansion with a symmetric form.

In the thermodynamical consideration, the entropy production is given by

$$\sigma_{e,\text{th}} = \sum_{i=1}^3 \mathcal{J}_i \frac{\mathcal{A}_i}{T}, \quad (4.6)$$

where

$$\mathcal{J}_1 = \kappa(\langle A \rangle - \langle X \rangle), \quad \mathcal{A}_1 = T \log \frac{\langle A \rangle}{\langle X \rangle}, \quad (4.7)$$

$$\mathcal{J}_2 = \kappa(\langle X \rangle - \langle Y \rangle), \quad \mathcal{A}_2 = T \log \frac{\langle X \rangle}{\langle Y \rangle}, \quad (4.8)$$

$$\mathcal{J}_3 = \kappa(\langle Y \rangle - \langle B \rangle), \quad \mathcal{A}_3 = T \log \frac{\langle Y \rangle}{\langle B \rangle}. \quad (4.9)$$

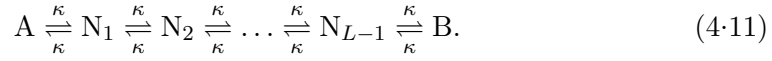
\mathcal{J}_i is the reaction rate of reaction i and \mathcal{A}_i is the affinity of reaction i . This expression is equivalent to Eq. (2.2). Near equilibrium, the entropy production is

$$\sigma_{e,\text{th}} \approx \frac{2\kappa\Omega(\langle a \rangle - \langle b \rangle)^2}{3(\langle a \rangle + \langle b \rangle)}. \quad (4.10)$$

The result of Eq. (4.5) disagrees with the thermodynamical result of Eq. (4.10).

4.2. One-dimensional diffusion system

In this subsection, a one-dimensional diffusion system is considered. The system is a pipe with the cross section Σ . This pipe is divided into L cells of length λ . Thus, the volume of each cell is $\Omega = \lambda\Sigma$. Particles exhibit a random walk between cells. All rate constants are given by κ . The reaction is represented as



The time evolution of the population N_i is determined by the following rate equation:

$$\dot{N}_i = \kappa(N_{i+1} - 2N_i + N_{i-1}), \quad (4.12)$$

and at both edges,

$$N_0 = A, \quad N_L = B. \quad (4.13)$$

At the edges, a constant number of particles is supplied by reservoirs. We denote the density of the particle in the i th cell by n_i , i.e., $n_i = N_i/\Omega$.

$$\begin{aligned} \dot{n}_i &= \kappa(n_{i+1} - 2n_i + n_{i-1}) \\ &\approx \kappa\lambda^2 \nabla^2 n. \end{aligned} \quad (4.14)$$

Thus, the spatial diffusion coefficient is given by

$$\mathcal{D} = \kappa\lambda^2. \quad (4.15)$$

Now let us consider the master equation for this system. The transition probabilities are given by

$$W(\dots, N_i, N_{i+1}, \dots \rightarrow \dots, N_i - 1, N_{i+1} + 1, \dots) = \kappa N_i, \quad (4.16)$$

$$W(\dots, N_i, N_{i+1}, \dots \rightarrow \dots, N_i + 1, N_{i+1} - 1, \dots) = \kappa N_{i+1}. \quad (4.17)$$

This problem was analyzed in the context of the fluctuation theorem.²⁴⁾ The steady solution of the master equation is multi-Poissonian.

$$P^{\text{st}}(N_1, N_2, \dots, N_{L-1}) = \prod_{i=1}^{L-1} e^{-\langle N_i \rangle} \frac{\langle N_i \rangle^{N_i}}{N_i!}. \quad (4.18)$$

The thermodynamical entropy production is given by

$$\sigma_{e,\text{th}} = \frac{\kappa(\langle A \rangle - \langle B \rangle)}{L} \log \frac{\langle A \rangle}{\langle B \rangle}. \quad (4.19)$$

This equation is equivalent to the Schnakenberg-Gaspard expression, Eq. (2.2). One can confirm by inserting Eq. (4.18) into Eq. (2.2), that Eq. (4.19) is satisfied. In the continuous limit, we have

$$\sigma_{e,\text{th}} = \Sigma \mathcal{D} \int_0^{L\lambda} dx \frac{|\nabla n(x)|^2}{n(x)}, \quad (4.20)$$

where Σdx is the volume element here. In the last line, we employed the linear approximation near equilibrium.

Using Eq. (2.19), the moments are calculated as

$$\mathbf{c}_{1,i} = \kappa(n_{i+1} - 2n_i + n_{i-1}), \quad (4.21)$$

$$\mathbf{c}_{2,i,i} = \kappa(n_{i+1} + 2n_i + n_{i-1}), \quad (4.22)$$

$$\mathbf{c}_{2,i,i+1} = \mathbf{c}_{2,i+1,i} = \kappa(n_i + n_{i+1}). \quad (4.23)$$

For \mathbf{c}_2 , other entries are zero. The matrices \mathbf{K}^{st} and \mathbf{D}^{st} are given by

$$\mathbf{K}^{\text{st}} = \kappa \begin{pmatrix} -2 & 1 & 0 & \cdots & \cdots & 0 \\ 1 & -2 & 1 & \cdots & \cdots & 0 \\ 0 & 1 & -2 & \ddots & \cdots & 0 \\ \vdots & \cdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & \cdots & 1 & -2 & 1 \\ 0 & \cdots & \cdots & 0 & 1 & -2 \end{pmatrix} \quad (4.24)$$

and

$$D_{i,i}^{\text{st}} = \frac{\kappa}{2}(n_{i-1}^{\text{st}} + 2n_i^{\text{st}} + n_{i+1}^{\text{st}}) = 2\kappa n_i^{\text{st}}, \quad (4.25)$$

$$D_{i,i+1}^{\text{st}} = D_{i+1,i}^{\text{st}} = -\frac{\kappa}{2}(n_i^{\text{st}} + n_{i+1}^{\text{st}}). \quad (4.26)$$

For \mathbf{D}^{st} , other entries are zero. We used the fact that the steady solution is given by

$$n_i^{\text{st}} = n_0 - i\lambda|\nabla n|. \quad (4.27)$$

The variance matrix $\boldsymbol{\sigma}^{\text{st}}$ and the circulation matrix $\boldsymbol{\alpha}$ are given by

$$\boldsymbol{\sigma}^{\text{st}} = \begin{pmatrix} n_1^{\text{st}} & 0 & 0 & \cdots & 0 \\ 0 & n_2^{\text{st}} & 0 & \cdots & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & \cdots & & n_{L-2}^{\text{st}} & 0 \\ 0 & \cdots & & 0 & n_{L-1}^{\text{st}} \end{pmatrix} \quad (4.28)$$

and

$$\begin{aligned} \boldsymbol{\alpha} &= \frac{1}{2}(\boldsymbol{\sigma}^{\text{st}} \widetilde{\mathbf{K}}^{\text{st}} - \mathbf{K}^{\text{st}} \boldsymbol{\sigma}^{\text{st}}) \\ &= \frac{\kappa\lambda\nabla n}{2} \begin{pmatrix} 0 & 1 & 0 & \cdots & \cdots & 0 \\ -1 & 0 & 1 & \cdots & \cdots & 0 \\ 0 & -1 & 0 & \ddots & \cdots & 0 \\ \vdots & \cdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & \cdots & -1 & 0 & 1 \\ 0 & \cdots & \cdots & 0 & -1 & 0 \end{pmatrix}. \end{aligned} \quad (4.29)$$

The entropy production for the corresponding Fokker-Planck equation is given by Eq. (3.12). Then we have

$$\begin{aligned}
 \langle \sigma_e \rangle &= -\text{Tr}(\boldsymbol{\alpha} \mathbf{R}^{\text{st}} \boldsymbol{\alpha} \mathbf{g}^{\text{st}}) \\
 &\approx \frac{\kappa \lambda^2 |\nabla n|^2}{4\bar{n}^2} \frac{2(L-2)(L-1)}{L} \\
 &= \frac{\mathcal{D}}{2\lambda\bar{n}} \int_0^{L\lambda} dx \frac{|\nabla n(x)|^2}{n(x)}. \quad (L \rightarrow \infty)
 \end{aligned} \tag{4.30}$$

This result does not agree with the thermodynamical result of Eq. (4.20). In particular, the order of Eq. (4.30) is different by a factor of $1/\Omega$ compared with that of Eq. (4.20) and the concentration dependence disagrees.

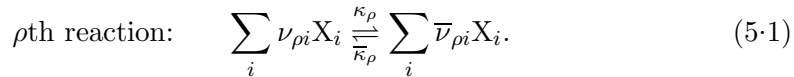
§5. Path weight principle

As shown in the previous section, the entropy production derived directly from our Fokker-Planck equation disagrees with that of the original master equation and the thermodynamical equation. This discrepancy should be examined.

First, let us consider the reason for this discrepancy. Our original master equation describes the phenomena of discrete jumps such as the occasional collisions in the chemical reaction system. On the other hand, the corresponding Fokker-Planck equation treats the averaged continuous evolution of the original physical random process. This relation is similar to that between a random walk and Brownian motion, which corresponds to the former. Note that the different random walks, say, (i) random jump $\pm\Delta$ at each mean interval τ_0 , and (ii) random jump $\pm 2\Delta$ at each mean interval $4\tau_0$, are described by the same Brownian motion with the diffusion coefficient $D = \Delta^2/2\tau_0$. However, the entropy production differs for each case, i.e., that of case (i) is four times larger than that of case (ii). This fact tells us that the Fokker-Planck equation and the Brownian motion cannot be used for the purpose of calculating the correct entropy production, at least, when the original master equation describes a discrete stochastic process. However, they accurately describe the long-time evolution of the probability itself due to the central limit theorem. The entropy production is due to the short-time behavior of fluctuations, i.e., the detailed imbalance relation. Entropy is created at each discrete jump process such as reactive collisions among atoms or molecules in the chemical reaction. Let us call these discrete jump process the elementary process of entropy production.

Second, let us introduce the *path weight principle*, which is a type of correspondence rule for overcoming this difficulty. The above consideration suggests that to calculate the correct entropy production in the present Fokker-Planck scheme, we should take account of the number of elementary processes included in a given continuous stochastic path.

For example, let us consider the following chemical reaction network,



The elementary random walk comprises each reactive collision which means that $\Delta Y_\rho = \pm 1$ in a mean interval $\kappa_\rho^{-1}(\bar{\kappa}_\rho^{-1})$, where Y_ρ is the reaction coordinate of the ρ th reaction defined by

$$\delta X_i = \sum_\rho (\bar{\nu}_{\rho i} - \nu_{\rho i}) \delta Y_\rho. \quad (5.2)$$

Using the reaction coordinates as the set of stochastic variables, the frequencies of the positive and negative reactions in the ρ th direction per unit time are related to the second moment of the transition probability,

$$2\Omega D_\rho'^{\text{st}} = W(\Delta Y_\rho = +1)(+1)^2 + W(\Delta Y_\rho = -1)(-1)^2, \quad (5.3)$$

when the reaction flow can be neglected in near-equilibrium situations. This condition will be satisfied in the linearized, local-equilibrium estimation below.

Thus, the diffusion constants directly give the number of elementary random walks in a unit time if the reaction rates satisfy $\kappa_\rho = \bar{\kappa}_\rho$. However, it is difficult to find a general correspondence rule for the population coordinate $\{X_i\}$ except for the following special cases.

5.1. One-dimensional diffusion system

In the diffusion model used in § 4, the rate constants κ_ρ 's are assumed to be a constant, κ , i.e.,

$$i\text{th reaction:} \quad N_i \xrightleftharpoons[\kappa]{\kappa} N_{i+1}, \quad (i = 0, 1, 2, \dots, L-1) \quad (5.4)$$

where $N_0 = A$ and $N_L = B$. The diffusion matrix in the reaction coordinates is given by a diagonal matrix $\{D_i'^{\text{st}}\delta_{ij}\}$, where

$$D_i'^{\text{st}} = \frac{\kappa}{2}(n_i^{\text{st}} + n_{i+1}^{\text{st}}), \quad (5.5)$$

with $n_i = N_i/\Omega$. The elementary process in this case is a jump of one particle in a given cell to the left or right cell in the mean interval time, κ^{-1} , that is, a uniform random walk in the one-dimensional real space. Therefore, at least in this special case, the number of elementary jump processes included in a continuous unit-time path in the i th direction is given by the ratio, $2\Omega D_i'^{\text{st}}/\kappa$. Then the correspondence rule in this case is given by

$$\dot{\eta}_i \longrightarrow 2\kappa^{-1}\Omega D_i'^{\text{st}}\dot{\eta}_i, \quad (5.6)$$

where $\eta_\rho = Y_\rho/\Omega$. Thus, the diffusion constant can be used for the path weight.

In the concentration space $\{n_i\}$, let us assume that the same correspondence rule can be applied in the principal-axis space where the diffusion matrix $\{D_{ij}^{\text{st}}\}$ is diagonalized, although we have no definite principle for determining the coefficient κ^{-1} itself in the present case. Note that this space is not necessarily equivalent to the reaction coordinate space $\{\eta_i\}$. We have the linear relations,

$$\dot{n}_i = \sum_\rho (\delta_{\rho, i-1} - \delta_{\rho, i}) \dot{\eta}_\rho, \quad (5.7)$$

and

$$D_{ij}^{\text{st}} = \sum_{\rho} (\delta_{\rho,i-1} - \delta_{\rho,i})(\delta_{\rho,j-1} - \delta_{\rho,j}) D_{\rho}^{\prime\text{st}}, \quad (5.8)$$

where $\delta_{\rho,i}$ is the usual Kronecker delta. However, this transformation is not represented as a square matrix, i.e., it is not invertible and not an orthogonal transformation.

Thus, we obtain a *hypothetical* correspondence rule in the concentration space

$$\dot{n}_i \longrightarrow \sum_j 2\kappa^{-1} \Omega D_{ij}^{\text{st}} \dot{n}_j. \quad (5.9)$$

Let us call this the *path weight principle*.

As a result, we have a corrected expression for the entropy production rate,

$$\langle \sigma_e \rangle' = -2\kappa^{-1} \Omega \text{Tr}(\boldsymbol{\alpha} \mathbf{g}^{\text{st}} \boldsymbol{\alpha}). \quad (5.10)$$

Here the prime means that the entropy production is modified by the path weight principle. Using the explicit forms of $\boldsymbol{\alpha}$ and \mathbf{g}^{st} in § 4, we obtain a final result,

$$\langle \sigma_e \rangle' = \Sigma \int_0^{L\lambda} \frac{\mathcal{D} |\nabla n(x)|^2}{n(x)} dx, \quad (5.11)$$

in the continuum limit $L \rightarrow \infty$, where $\mathcal{D} = \kappa\lambda^2$ is the spatial diffusion constant. This coincides exactly with the thermodynamic result, i.e., Eq. (4.20).

5.2. Chemical reaction network

The path weight principle may also be applied to the simple chemical reaction ($L = 3$) in § 4.1. A simple result for the evaluation of the entropy production is given by

$$\langle \sigma_e \rangle' = \frac{2\kappa\Omega(\langle a \rangle - \langle b \rangle)^2}{9(\langle a \rangle + \langle b \rangle)}, \quad (5.12)$$

in a symmetrized form near equilibrium. Compared with Eq. (4.10), there is a difference of a factor of 1/3.

The reason for this is evident. We should treat the boundary effect more carefully for finite L . In the present case there are three different random walks in the xy -plane, i.e., two boundary modes \dot{Y}_0 along the x -axis and \dot{Y}_2 along the y -axis in addition to the diagonal mode \dot{Y}_1 in the direction $(1, -1)$. Therefore, the elementary processes are not isotropic in the xy -plane.

Instead of performing this ambiguous transformation, the reason for the factor of 1/3 may be that the irreversible circulations corresponding to both end reactions have not been taken into account in the present scheme. It can be easily shown that this factor of 1/3 is removed when the variables A and B are added to the set of stochastic variables as

$$\dot{A} = \kappa(X - A) - c, \quad (5.13)$$

$$\dot{X} = \kappa(A - 2X + Y), \quad (5.14)$$

$$\dot{Y} = \kappa(X - 2Y + B), \quad (5.15)$$

$$\dot{B} = \kappa(Y - B) - c', \quad (5.16)$$

where c and c' are parameters controlled by external equilibrium reservoirs to keep A and B constant. Here $c = \kappa(\langle X \rangle - A)$ and $c' = \kappa(\langle Y \rangle - B)$. Except for the matrix \mathbf{K}^{st} , which is modified slightly to

$$\mathbf{K}^{\text{st}} = \kappa \begin{pmatrix} -1 & 1 & 0 & 0 \\ 1 & -2 & 1 & 0 \\ 0 & 1 & -2 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}, \quad (5.17)$$

the other quantities are exactly the same as those given in § 4.2 for $L - 1 = 4$.

§6. Concluding remarks

We have shown that the entropy production of the Fokker-Planck equation derived from the master equation differs from that for the original master equation. The reason for this is clearly due to the fact that the master equation treats discrete events, but the Fokker-Planck equation is an approximation of the master equation. In the Fokker-Planck equation, the original discrete events are smoothed out. To evaluate the entropy production, one has to recover the discreteness of the events in the treatment of the corresponding Fokker-Planck equation. To overcome this problem, we have proposed the *path weight principle*. The entropy production from the corresponding Fokker-Planck equation is modified by multiplying by the diffusion coefficient. For two simple examples, it has been demonstrated that the path weight principle yields the entropy production for the original master equation.

At present, we do not know whether or not the path weight principle can be applied to any type of master equation. However, we believe that the path weight principle can be applied, at least, to the cases in which jumps in the transitions are small compared with Ω , namely $|\Delta| \sim 1$.

Acknowledgements

The authors are grateful to Professor K. Kitahara for enlightening discussions and continuous encouragement.

References

- 1) L. Onsager, Phys.Rev. **37** (1931), 405; *ibid.* **38** (1931), 2265.
- 2) S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
- 3) R. Kubo, J.Phys.Soc.Jpn. **12** (1957), 570.
- 4) D. J. Evans, E. G. D. Cohen and G. P. Morris, Phys.Rev.Lett. **71** (1993), 2401 [Errata; **71** (1993), 3616].
- 5) D. J. Evans and D. J. Seales, Phys.Rev.E **50** (1994), 1645.
- 6) G. Gallavotti and E. G. D. Cohen, Phys.Rev.Lett. **74** (1995), 2694; J.Stat.Phys. **80** (1995), 931.
- 7) J. Kurchan, J. of Phys.A **31** (1998), 3719.
- 8) J. L. Lebowitz and H. Spohn, J.Stat.Phys. **95** (1999), 333.
- 9) C. Maes, J.Stat.Phys. **95** (1999), 367.
- 10) J. Schnakenberg, Rev.Mod.Phys. **48** (1976), 571.
- 11) P. Gaspard, J.Stat.Phys. **117** (2004), 599 [Errata; **126** (2006), 1109].

- 12) R. Kubo, K. Matsuo and K. Kitahara, J.Stat.Phys. **9** (1973), 51.
- 13) K. Tomita and H. Tomita, Prog.Theor.Phys. **51** (1974), 1731 [Errata; **53** (1975), 1546b].
- 14) N. G. van Kampen, Can.J.Phys., **38** (1961), 551.
- 15) L. Onsager and S. Machlup, Phys.Rev. **91** (1953), 1505.
- 16) S. Machlup and L. Onsager, Phys.Rev. **91** (1953), 1512.
- 17) K. Tomita, T. Ohta and H. Tomita, Prog.Theor.Phys. **52** (1974), 737.
- 18) T. Sakaue and T. Ohta, arXiv:0710.2717.
- 19) T. Taniguchi and E. G. D. Cohen, J.Stat.Phys. **126** (2007), 1.
- 20) T. Taniguchi and E. G. D. Cohen, arXiv:0706.1999.
- 21) T. Taniguchi and E. G. D. Cohen, arXiv:0708.2940, (2007).
- 22) U. Seifert, Phys. Rev. Lett. **95** (2005), 040602.
- 23) V. Y. Chernyak, M. Chertkov and C. Jarzynski, J.Stat.Mech.: Theor. and Exper. (2006), P08001.
- 24) D. Andrieux and P. Gaspard, J.Stat.Mech.: Theor. and Exper. (2006), P01011.